



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁵ : C11D 3/43, C23G 5/06	A1	(11) International Publication Number: WO 92/18600 (43) International Publication Date: 29 October 1992 (29.10.92)
(21) International Application Number: PCT/US92/02760 (22) International Filing Date: 6 April 1992 (06.04.92) (30) Priority data: 683,240 10 April 1991 (10.04.91) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: BOSSCHER, Douglas, J. ; HENDRICKSON, Carol, E. ; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: BJORKMAN, Dale, A. et al.; Office of Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: LOW VOC CLEANING COMPOSITIONS AND METHODS (57) Abstract <p>A method of removing residue from hard surfaces utilizes an oil-in-water microemulsion by applying to such surfaces an effective amount of a composition comprising an organic solvent or solvent blend having a solubility parameter of between about 6.9 and 8.9 (cal/cm³)^{1/2}, sufficient surfactant to support a stable microemulsion, and water in an amount sufficient to provide a total VOC content of less than 200 grams/liter. The microemulsion is allowed to soften and otherwise ease removal of the silicone wax, grease, grime, and the like from the surface. The microemulsion and the residue to be cleaned from the surface are removed from the surface by wiping with a dry wiping material. Compositions are also provided.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	RU	Russian Federation
CG	Congo	KP	Democratic People's Republic of Korea	SD	Sudan
CH	Switzerland	KR	Republic of Korea	SE	Sweden
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
DE	Germany	MC	Monaco	TC	Togo
DK	Denmark			US	United States of America

- 1 -

LOW VOC CLEANING COMPOSITIONS AND METHODSBACKGROUND

5

Field of Invention

This invention relates to compositions and methods for removing silicone wax, grease, grime, adhesives and the like from hard surfaces such as automobile finishes.

Description of the Art

Currently, contaminants are removed from hard surfaces such as automobile finishes with cleaning fluids that are predominately organic solvents. These solvents are now being regulated because of their effect on air quality. Specifically, the South Coast Air Quality Management District and Bay Areas of California have issued rules defining the amount of Volatile Organic Compounds (VOCs) which may be present in certain materials whose vapors may be discharged into the atmosphere. Additionally, organic solvents suffer from the disadvantage that they may evaporate before there is an opportunity to wipe it off. Premature evaporation may leave soil residues on the surface to be cleaned.

U.S. Patent No. 4,446,044 to Rutkiewicz, et. al. describes a water-in-oil emulsion, used as a cleaning fluid for automotive finish surfaces. Rutkiewicz, et. al. make the explicit statement at column 3, lines 23-26 that "in order for this particular emulsion to be efficacious as a cleaner, it is necessary that the water, not the organic solvent, constitute the internal phase." This suggests that the emulsion must be of the water-in-oil type for effective cleaning.

U.S. Patent No. 3,983,047 to Vinson describes a decal removal composition for loosening adhesive bonded to an airplane. The composition contains mostly organic solvent well above the regulated VOC limit and
5 is a solvent mixture.

U.S. Patent No. 4,146,499 to Rosano discloses a method of preparing microemulsions for a wide variety of applications including the use of hydrophobic substance such as hydrocarbon substances including
10 mineral spirits for "their ability to dissolve most hydrophobic substance."

U.S. Patent No. 4,909,962 to Clark describes a composition used primarily for laundry pre-spotting that is a microemulsion comprising organic solvent and
15 a selection of nonionic surfactants and cosolvents. Component C of this composition is a supplementary nonionic surfactant comprising an amine oxide or an alkyl phenol ethoxylate. See especially col. 2, line 59 and Examples 7 and 8 at col. 8. These compositions are
20 specifically intended to be used on fabrics that will be followed by a regular washing, thereby infinitely diluting the composition with a water ratio of at least 100 parts water to 1 part composition. The optional use of these compositions as all-purpose cleaners for
25 hard surfaces is disclosed at column 3, lines 21 to 30.

U.S. Patent No. 4,370,174 to Brathwaite, Jr. discloses a method for removing adhesive residues using an emulsion cleaner. The composition used comprises an organic solvent, a minor amount of an inorganic solid
30 absorbent powder, an water-in-oil surfactant and an oil-in-water surfactant sufficient to reverse the emulsion to a water external phase upon addition of water. The emulsion was initially provided in an oil external phase because it was believed that this was
35 necessary to insure that the organic solvent was exposed to the adhesive residue. These compositions are applied to flooring surfaces as a preparation for subsequent application of adhesives. The compositions

- 3 -

are poured directly on the surface to be cleaned and allowed to dissolve the adhesive for about 10 to 30 minutes.

There is a need in the art for a composition
5 to clean difficult-to-remove contaminants from hard surfaces safely while at the same time satisfying stringent VOC requirements. Such compositions preferably should be easily removed from the surface to be cleaned so as not to leave any residue. Water-based
10 cleaners may be washed from the surface to be cleaned with excess water, but this is undesirable because this process requires an additional step and can leave water running from the interstices of joints in the structure that must be dried before painting. Water flushing is
15 particularly undesirable when cleaning automobile surfaces for refinishing.

Summary of the Invention

The present invention provides a method of
20 removing silicone wax, grease, grime, adhesives and other such residues from hard surfaces such as tile, windows, plastic, metal and painted surfaces with an oil-in-water microemulsion comprising applying to such surfaces an effective amount of a composition
25 comprising an organic solvent or solvent blend having a solubility parameter of between about 6.9 and 8.9 $(\text{cal}/\text{cm}^3)^{1/2}$, sufficient surfactant to support a stable microemulsion, and water in an amount sufficient to provide a total VOC content of less than 200
30 grams/liter. The microemulsion is allowed to soften and otherwise ease removal of the silicone wax, grease, grime, and the like from the surface. The microemulsion and the residue may be removed from the surface by wiping with a dry wiping material.

35 The microemulsion used in the present method yields surprising cleaning power with a small amount of volatile organic solvent, and without the need for

large amounts of detergent, harsh pH conditions or the like.

Detailed Description of Presently Preferred Embodiments

5 The method of the present invention is specifically adapted to the particular performance requirements of the operation to be performed. Thus, where the surface to be cleaned is soiled by oil, grease, wax or the like and is to be repainted or
10 otherwise refinished, it is particularly important to provide cleaning that will leave no trace of residue of either the soil or the cleaning agent itself. Such cleaning is particularly important in the repainting of automobile surfaces. Such residues will lead to "fish
15 eyes," or noticeable bumps in the painted surface. The microemulsion, when used in accordance with the present invention, may be applied to the surface to be treated and effectively wiped away using only a dry wiping material. No additional cleanup, such as a water wash,
20 is required to remove any trace cleaner. When a surface that is soiled with adhesive is to be cleaned, the standard of desired cleaning may not need to be as high as for surfaces to be repainted, because adhesive will likely be applied to the same surface. In such
25 applications, however, good cleaning is still important to avoid adhesive failure due to adhesive or surfactant residue remaining on the surface. Here again, the microemulsion is applied to the surface to be treated and effectively wiped away using only a dry wiping
30 material without additional cleanup.

 The oil-in-water microemulsion used in the present invention provides good cleaning action while at the same time satisfying environmental standards for VOCs. The organic solvent also does not evaporate
35 rapidly because it is contained within discontinuous droplets distributed in the continuous aqueous phase, and is not present in quantity at the liquid-air interphase. The lower evaporation rate of the organic

- 5 -

solvent is further advantageous, because tenacious waxy or adhesive residues are allowed to soak in the solvent prior to removal. Environmental compatibility of the present microemulsion may be further improved with the
5 choice of nontoxic organic components and biodegradable surfactants. Judicious choice of components also may render the microemulsion nonflammable for easier compliance with shipping regulations.

Residue may be more easily removed from the
10 surface to be cleaned using the present oil-in-water microemulsions by simple dry wiping techniques than using a solvent-based or water-in-oil based system. If desired, the present microemulsion may alternatively be removed by water washing techniques, because the
15 microemulsion is water-dilutable. Water washing is not practical in solvent-based or water-in-oil based systems. Ease in cleanup provides significant advantages both in labor-saving and a more acceptable final product.

20 The microemulsion used in the present invention is an oil-in-water microemulsion. Such microemulsions typically contain dispersed droplets of oil in the range of 50-1500A in diameter, which is visibly transparent or translucent. The microemulsion
25 is formed spontaneously, i.e., without any energy input, with the proper selection of oil, water and surfactant components.

The organic solvent component of the microemulsion is an organic solvent or solvent blend
30 having a solubility parameter of between about 6.9 and 8.9. The specific solvent or solvent blend and the concentration of the solvent to be used is selected on the basis of the proposed application. In case of applications of cleaning silicone wax, grease, grime or
35 the like, a low concentration of a mild hydrocarbon such as odorless mineral spirits is most suitable for cost concerns and minimal effect on fresh paint finishes. In case of adhesive remover applications or

other such applications where a more aggressive cleaning action is required, a higher concentration of a more aggressive organic solvent or solvent blend is preferred. The solvent selected should preferably have
5 a solubility parameter of between about 7.5 and 8.9 $(\text{cal}/\text{cm}^3)^{1/2}$. Preferred aggressive solvents or solvent blends comprise at least 5% by weight of the solvent ingredient of a polar or aromatic component. Examples
10 of such a polar component include butyl acetate, acetone, glycol ether, alcohols or the like. The aromatic component may be toluene, xylene, naphthalene or the like.

Suitable microemulsions typically comprise:

- a) an organic solvent or solvent blend
15 having a solubility parameter of between about 6.9 and 8.9 $(\text{cal}/\text{cm}^3)^{1/2}$,
- b) sufficient nonionic surfactant or surfactant blend to maintain a microemulsion, and
- c) water in an amount sufficient to provide
20 a total VOC content of less than 200 grams/liter.

More typically, the microemulsion comprises a blend of surfactants to enhance stability of the composition. Blends of surfactants are generally more efficient in providing stability, and thus need not be
25 provided in as large amounts as a single surfactant. The surfactants typically are of diverse chemical classes, selected from cationic, zwitterionic, anionic and nonionic surfactants. Preferably, the surfactants are selected from the nonionic surfactants, together
30 with another surfactant selected from cationic, zwitterionic and anionic surfactants.

The combination of cationic or zwitterionic surfactants with nonionic surfactants provides a wide range of temperature stability to the microemulsion and
35 a low surfactant concentration.

The surfactants serve both as emulsifiers and, to some extent, as cleaning agents. The surfactant combination is preferably chosen based on

- 7 -

its removability from the surface or compatibility with subsequently applied paints and biodegradability. The preferred HLB of the nonionic surfactant is determined by the choice of organic solvent components and is
5 selected to be higher than 7 to enable a spontaneously formed oil-in-water emulsion.

Cationic or zwitterionic surfactants, such as amines and their salts, quaternary ammonia salts, amine oxides, or other cationic surfactants known in the art,
10 may be used. Alkylamine oxides, such as cocadimethylamine oxide or lauryldimethamine oxide, are preferred because of their low toxicity.

Typical nonionic surfactants that may be used in the microemulsions of the present invention include
15 the polyoxyethylene surfactants, such as polyethoxylated alkyphenols and polyethoxylated linear or branched primary or secondary alcohols; the carboxylic acid esters, such as glycerol esters, polyoxyethylene esters, ethoxylated anhydrosorbitol
20 esters, ethoxylated natural fats, oils and waxes and glycol esters of fatty acids; the carboxylic amides, such as diethanolamine condensates, monoalkanolamine condensates, polyoxyethylene fatty acid amides; and the polyalkylene oxide block copolymers, such as PluronicTM.
25 line of surfactants from BASF Corp. Polyethoxylated linear alcohols, such as NeodalTM manufactured by Shell Chemicals and TergitolTM manufactured by Union Carbide Company, are preferred as most biodegradable.

Most preferably, the microemulsion also
30 comprises a co-surfactant to aid the solubilization of the surfactants in the solvent, to minimize gelation during phase transition, and to provide transparency and low viscosity of the microemulsion. The co-surfactant is chosen based on its polarity as well
35 as low toxicity and flammability. Mid chain length alcohols; such as n-propanol, n-butanol, pentanol, glycols; such as propylene glycol, or glycol ethers; such as dipropylene glycol methyl ether, diethylene

glycol butyl ether, propylene glycol methyl ether, ethylene glycol butyl ether can be used. The use of an alcohol which also acts as a solvent is additionally advantageous especially in case of the adhesive remover application. An inflammable, low toxic glycol ether, such as dipropylene monoethyl ether, is preferred especially in the adhesive remover formulation which has a higher concentration of organic components.

To formulate experimental microemulsions according to the present invention, the solvent or solvent blend is mixed with an amount of cosurfactant equal or slightly less than the amount of surfactant to be used in the ultimate composition. The cationic and nonionic surfactants are added to the solvent mixture, and the resultant mixture stirred well. Water is added in aliquots with gentle stirring after each addition until the viscosity has increased and subsequently decreased to indicate a phase transition from water-in-oil to oil-in-water. From this point on, water can be added rapidly in an amount to provide the concentration desired.

The appropriate ratio of surfactants and amount of cosurfactant is determined through routine experimentation, reducing the amount of comparatively expensive ingredients as taught herein as possible for the particular solvent or solvent blend used. The ratio of cationic to nonionic surfactant can be adjusted to minimize the total amount of necessary surfactant. Generally, when less cationic surfactant is used, the total amount of surfactant must be increased. The cosurfactant is preferably added before the addition of water because it aids the solubilization of the surfactants in the solvent and minimizes gelation during the phase transition. The amount of cosurfactant to be used is adjusted to provide transparency and low viscosity. If the amount of necessary cosurfactant exceeds the desired VOC, the formulation is adjusted by changing the ratios of

- 9 -

surfactants in the formulation. Once the ratio of surfactant and cosurfactant has been established, the concentration of each component can be lowered or raised in relationship to the solvent to optimize
5 stability and performance.

Once a satisfactory formulation for the microemulsion has been determined, usually no special techniques for mixing are required. All of the ingredients may be added in any order and mixed to form
10 the microemulsion as taught herein.

Preferred microemulsions comprise by weight:

- a) 5-15% of an organic solvent or solvent blend having a solubility parameter of between about 6.9 and 8.9 (cal/cm³)^{1/2},
- 15 b) 8-12% of a cationic or zwitterionic surfactant,
- c) 4-8% of a nonionic surfactant or surfactant blend having an HLB of between about 7.5 and 10,
- 20 d) 1-5% of a co-surfactant, and
- e) 50-82% of water, such that the total VOC content of the microemulsion is less than 200 grams/liter.

Where the microemulsion is to be used for
25 cleaning silicone wax, grease, grime, and the like from hard surfaces to be repainted, a milder, less expensive yet effective cleaning solution is preferably provided by a composition comprising by weight:

- 30 5-8% aliphatic organic solvent,
- 1-3% co-surfactant,
- 3-5% amine oxide surfactant,
- 2-4% nonionic surfactant having an HLB of between 7.5 and 10, and
- 35 80-89% deionized water to total 100%.

Where the microemulsion is to be used for cleaning adhesives from hard surfaces, a stronger

cleaning solution is preferably provided by a composition comprising by weight:

5	12-15%	organic solvent having at least 5% aromatic or polar components,
	1-4%	co-surfactant,
	8-12%	amine oxide surfactant,
	5-7%	nonionic surfactant having an HLB of between 7.5 and 10, and
10	62-74%	deionized water to total 100%.

The microemulsion can be applied with a pump spray, aerosol, or by wiping a rag, or preferably a highly absorbent, nonwoven pad, which can be rubbed
15 onto the surface to be cleaned. Because of its low volatility, the microemulsion can be left on the surface to soak the contaminant if necessary. A clean rag or nonwoven pad can be used to wipe up the dissolved soil or, optionally, the surface can be
20 rinsed with water. To assure that all of the residue is actually removed and not merely redeposited on drying of the cleaner, physical wiping of the substrate is preferred. The characteristics of the wiping material are chosen to act as a carrier for the
25 application of the microemulsion to the surface to be cleaned. This material must be soft enough as not to scratch the surface, non-linting and absorbent enough to hold sufficient quantities of soil/microemulsion. The preferred wiping material is a surfactant-treated
30 polypropylene nonwoven wiper.

Adhesive can be quickly removed if its bulk has been previously removed mechanically. Preferably, the bulk of the adhesive is removed with a 3M Striping and Molding Adhesive Removal Disc, which is a
35 commercially available elastomeric disc that is rotatable about its axis. These disks rub off adhesive residues without harming the underlying finish by frictional contact with the peripheral surface of the

- 11 -

disk. During the removal of adhesive step, a portion of the peripheral surface of the disk is attributed to provide a renewed peripheral surface of the elastomer. After cleaning with the emulsion according to the
5 method of the present invention, the surface is surprisingly clean and requires no further cleaning step before repainting or reapplying decals, molding, striping, etc.

The following non-limiting examples are
10 provided to illustrate the present invention.

EXAMPLE 1

A transparent microemulsion was prepared by combining the following ingredients and stirring.

15

6.1 wt% Odorless Mineral Spirits (Unocal
1241, Union Oil Co.) Unocal
Corporation.

1.5 n-propanol

20

4.4 Mackamine LO 30% active (a
laurylamine oxide surfactant from
McIntyre Chem Co.)

2.4 Tergitol 15-S-3 (a nonionic
surfactant from Union Carbide
Corporation)

25

85.5 deionized water

EXAMPLE 2

A transparent microemulsion was prepared by
30 combining the following ingredients and stirring.

14.2 wt% Unocal 75 Mineral Spirits
(Union Oil Co.)

5.6 Dipropylene glycol methyl
ether

35

13.0 Mackamine LO 30% active

- 12 -

6.0	Neodal 23-3 (a nonionic surfactant from Shell Oil Co.)
61.2	deionized water

5

EXAMPLE 3

The composition of example 3 was used to remove the following adhesives baked 150 F three hours onto a painted test panel that is a cold rolled steel panel painted with a base coat/clear coat paint system from DuPont, commercially available from Advanced Coating Technology, Inc.

15	ScotchMount	06378
	ScotchMount	06381
	ScotchCal	A-1
	3M Weather Stripping	
	Adhesive	08011
	3M General Trim Adhesive	

These adhesives represent acrylate, styrene butadiene, and Neoprene type adhesives. The bulk of adhesive was removed with the SCOTCH-BRITE Molding Adhesive and Stripe Removal Discs, deliberately leaving white smears of adhesive to better challenge the microemulsion adhesive cleaner. A hand size pad of nonwoven material as moistened with the microemulsion and rubbed for a maximum of five minutes or until the adhesive was removed from an approximate 3.5 square inch area.

30

EXAMPLE 4

The following microemulsions were prepared and used to remove the following adhesives after the bulk of adhesive was removed with 3M Striping and Molding Adhesive Removal Discs. Smears of adhesive were deliberately left on the surface to be cleaned to better challenge the power of the microemulsion adhesive remover.

-13-

Amount of Each Component in Weight %
(balance is water)

Oil	n-propanol	Triton TM N-57	Mackamine TM Lo	Triton TM X-35	Mins. for removal
Unocal 1241 (a)	14.2	3.6	1.0	10.2	4.6
3M GPAC (b)	14.2	3.6	1.0	12.9	1.2
Unocal 75 (c)	14.2	3.6	6.0	7.6	--
Isopar H (d)	14.2	3.6	1.2	10.2	4.6
duPont Mid Temp Reducer (e)	15.4	0.6	2.2	7.6	--
PPG Warm Temp Reducer (f)	15.0	3.0	2.0	8.6	--
Dibutyl Esters	14.2	3.6	1.0	10.2	4.6
Xylene/mineral spirits 50/50	13.5	3.5	1.1	10.2	4.7

- (a) a nonionic surfactant commercially available from Union Carbide Corporation.
 (b) Odorless mineral spirits commercially available from Unocal Corporation
 (c) xylene/petroleum distillates commercially available from 3M Company.
 (d) 7.5% aromatic mineral spirits commercially available from Unocal Corp.
 (e) a mixture of alkanes commercially available from Exxon Corporation.
 (f) a mixture of butyl acetate, acetone, toluene, glycol ethers, diisobutyl ketone, VM&P
 naphtha and aromatic hydrocarbons commercially available from E.I. duPont deNemours &
 Co., Inc.
 (g) a mixture of petroleum distillates, toluene, xylene, esters and glycol esters
 commercially available from PPG Industries, Inc.

This example shows the variety of organic solvents that can be microemulsified with this basic formulation and their comparative efficiencies.

5

EXAMPLE 5

The following microemulsions were prepared using 14.2 wt. % Unocal 75 solvent, the surfactants listed below and the balance of water.

10

Amount of Each Component in weight %

	<u>Cosurfactants</u>		<u>Surfactant 1</u>		<u>Surfactant 2</u>		
	a)	Propylene Glycol	4.4	Triton N-57	6.0	Mackamine LO	7.6
15	b)	DiPropylene Glycol	4.6	Triton N-57	6.0	Mackamine LO	7.6
	c)	Diethylene Glycol butyl ether	3.5	Triton N-57	6.0	Mackamine LO	6.0
20	d)	N-propanol	3.6	Triton N-57	6.0	Mackamine LO	7.6
25							

EXAMPLE 6

The following microemulsions were prepared using several more biodegradable nonionic surfactants and balanced with water.

30

In the table below, the abbreviations are:

U75 = Unocal 75, 7.5% aromatic mineral spirits commercially available from Unocal Corporation.

35

U1241 = Unocal 1241, odorless mineral spirits commercially available from Unocal Corporation.

DPM = dipropylene glycol methyl ether.

n-pro = n-propanol.

40

T15-S-3 = Triton 15-S-3, a nonionic surfactant from Union Carbide Corporation.

Neo 91-6 = Neodal 91-6, a nonionic surfactant from Shell Oil Co.

- 15 -

T15-S-5 = Triton 15-S-5, a nonionic surfactant from Union Carbide Corporation.

Neo 23-3 = Neodal 23-3, a nonionic surfactant from Shell Oil Co.

5

Amount in weight %

10

Oil		cosurfactant		Macka- mine LO	surfactant A		surfactant B
U75	14.2	DPM	5.6	13.6	T15-S-3	7.2	0
U75	14.2	DPM	4.5	10.0	T15-S-5	12	0
U75	14.2	DPM	5.6	10.2	Neo91-6	0.5	Neo23-2 5.5
U75	14.2	DPM	5.6	13.0	Neo23-3	6.0	0
U1241	6.2	n-pro	1.5	4.4	T15-S-3	2.4	0
U1241	6.2	n-pro	1.5	4.4	Neo23-3	2.4	0

15

TEST PROTOCOL

The ability of compositions to clean a silicone and wax contaminated automobile panel was evaluated by the following technique. Commercial
 20 silicone and/or wax containing polishes were applied to painted panels according to directions of the manufacturer to provide a contaminated surface. The microemulsion was applied to a clean, dry pad, wiped onto the contaminated surface and wiped off with a
 25 second clean, dry pad. The panel was then repainted and the quality of the paint finish evaluated by counting the number of "fish eye" caused by poor filming and adhesion and by the cross-hatch adhesion test (ASTM D3359). A control section was cleaned by
 30 Ditzler DX330, a commercial, pure solvent prep solvent.

Panel Preparation

Painted steel panels, 25.4 cm x 122 cm, were waxed with either DuPont Rain DanceTM paste wax or 3M Liquid Polish, PN 05993. The waxed panels were
 5 conditioned at room temperature for 7 days. Panels were then taped off with 2.54 cm wide plastic tape into separate 22 cm x 28 cm sections, and each section was cleaned as according to manufacturer's specification.

10 Specifically,

Ditzler DX-330 - apply about 4 grams to Scott WypAllTM towel and apply to wax panel - wipe off with clean, dry Scott WypAll.

Example 1 - apply about 5 grams to Scott
 15 WypAll towel and apply to waxed panel - wipe off with clean, dry WypAll towel.

ACME Aqua KlixTM - same as Example 1.

DuPont Prep Solvent II - apply about 5 grams with Scott WypAll towel - let stand about 2 minutes -
 20 remove with wet WypAll towel followed by dry WypAll towel.

BASF - same as DuPont Prep Solvent II, except use two wet wipes.

25 RESULTS

"Fish Eyes" Per 28 cm x 22 cm Panel

	<u>Rain Dance</u>	<u>Liquid Polish</u>
Example 1	26.5	27
DuPont	24.3	29.7
30 BASF	26.7	29.7
ACME	25.0	37.3
Ditzler	4.7	11.7

The best cleaner is Ditzler DX-330, which is
 35 a standard solvent cleaner and does not comply with VOC standards. Example 1 compares favorably with the other low VOC cleaners, but accomplishes this cleaning in one step rather than two steps.

- 17 -

Cross Hatch Adhesion

Two cross hatch sections performed, one with a light scratch and one with a deep scratch in accordance with ASTM D3359. The performance evaluation used the following criteria:

- Good - No top paint removed from paint directly covered
- either scratch.
- 10 Fair - Some top coat removed from deep scratch only.
- Poor - Some top coat paint removed from both scratch areas.
- V. Poor - total top coat paint removed over all taped area.

15

	<u>Cleaner</u>	<u>Liquid Polish</u>	<u>Rain Dance</u>
	Example 1	3 Good	3 Good; 1 Fair-Poor
	Ditzler	3 Good	3 Good
	DuPont	3 Good; 1 Poor	1 Good; 1 Poor, 1 Very Poor
20	BASF	2 Good; 1 Poor	1 Poor; 2 Very Poor
	ACME	2 Good; 1 Fair	2 Good; 1 Fair

Using this test, the composition of Example 1 performed as well or better than other low VOC prep solvents.

25

Fresh Paint Attack

24 hour old DuPont Centari Acrylic Enamel painted panels were used to test solvent attack by prep solvents.

30

Example 1 - no attack after 1 minute.

3M General Purpose Adhesive Cleaner - swells paint 5-10 seconds.

DuPont Prep Sol II 39295 - attacks, swells paint.

35 ACME Aqua Klix - very slight attack.

BASF 905 - attacks, swells paint.

Stability, Particle Size and Flash Point

The stability of the experimental
5 microemulsions of the present invention was tested by
subjecting samples to a minimum of three freeze-thaw
cycles and to a minimum of one week at 50 C. Although
some samples would separate into distinct phase, the
transparent microemulsion could be restored with mild
10 shaking.

Droplet particle size was determined by
dynamic light scattering using a Malvern Photon
Correlation Spectrometer.

Flash point measurements were made according
15 to the Tag closed cup method in accordance with
ASTM D 56.

As will be apparent to those skilled in the
art, various other modifications can be carried out
from the above disclosure without departing from the
20 spirit and scope of the invention.

- 19 -

CLAIMS:

1. A method of cleaning silicone wax, grease, grime, adhesives and the like from a hard surface in need of cleaning comprising
 - 5 i) applying to such surface an effective amount of a composition comprising an organic solvent or solvent blend having a solubility parameter of between about 6.9 and 8.9 $(\text{cal}/\text{cm}^3)^{1/2}$, sufficient surfactant to support a stable microemulsion, and water
10 in an amount sufficient to provide a total VOC content of less than 200 grams/liter;
 - ii) allowing said composition to soften and otherwise ease removal of said silicone wax, grease, grime, and the like from the surface; and
15 iii) wiping said composition and silicone wax, grease, grime, and the like from the surface with a dry wiping material.
2. The method of claim 1, wherein said
20 solvent or solvent blend has a solubility parameter of between about 7.5 and 8.9.
3. The method of claim 1, wherein said solvent or solvent blend is at least 5% by weight polar
25 or aromatic components.
4. The method of claim 1, wherein said microemulsion comprises:
 - a) an organic solvent or solvent blend
30 having a solubility parameter of between about 6.9 and 8.9 $(\text{cal}/\text{cm}^3)^{1/2}$,
 - b) sufficient nonionic surfactant or surfactant blend to maintain a microemulsion, and
 - c) water in an amount sufficient to
35 provide a total VOC content of less than 200 grams/liter.

5. The method of claim 4, wherein said microemulsion further comprises an additional surfactant selected from cationic, zwitterionic and anionic surfactants.

5 6. The method of claim 5, wherein said microemulsion further comprises a co-surfactant.

7. The method of claim 1, wherein said microemulsion comprises by weight:

10 a) 5-15% of an organic solvent or solvent blend having a solubility parameter of between about 6.9 and 8.9,

b) 8-12% of a cationic or zwitterionic surfactant,

15 c) 4-8% of a nonionic surfactant or surfactant blend having an HLB of between about 7.5 and 10,

d) 1-5% of a co-surfactant, and

e) 50-82% of water, such that the
20 total VOC content of the microemulsion is less than 200 grams/liter.

8. A method of cleaning silicone wax, grease or grime according to claim 1, wherein said
25 microemulsion comprises by weight:

5-8% aliphatic organic solvent,

1-3% co-surfactant,

3-5% amine oxide surfactant,

2-4% nonionic surfactant having an HLB
30 of between 7.5 and 10, and

80-89% deionized water to total 100%.

9. A method of cleaning adhesives according to claim 1, wherein said microemulsion comprises by
35 weight:

12-15% organic solvent having at least 5% aromatic or polar components,

1-4% co-surfactant,

- 21 -

8-12% amine oxide surfactant,
5-7% nonionic surfactant having an HLB
of between 7.5 and 10, and
62-74% deionized water to total 100%.

5

10. The method of claim 1, wherein said organic solvent or solvent blend is selected from the group consisting of odorless mineral spirits.

10

11. The method of claim 1, wherein said organic solvent or solvent blend is selected from the group consisting of aromatic mineral spirits, toluene, xylene and mixtures thereof.

15

12. The method of claim 7, wherein said cationic or zwitterionic surfactant is selected from the group consisting of alkylamine oxides.

13. The method of claim 7, wherein said cationic or zwitterionic surfactant is selected from the group consisting of cocadimethylamine oxide and lauryldimethamine oxide.

14. The method of claim 4, wherein said nonionic surfactant is selected from the group consisting of polyethoxylated linear, primary alcohols.

15. The method of claim 6, wherein said co-surfactant is selected from the group consisting of n-propanol, n-butanol, pentanol, propylene glycol, dipropylene glycol methyl ether, diethylene glycol butyl ether, propylene glycol methyl ether, ethylene glycol butyl ether and dipropylene monoethyl ether.

35

16. The method of claim 15, wherein said co-surfactant is selected from the group consisting of n-propanol and dipropylene glycol methyl ether.

17. The method of claim 1, further comprising the step of previously removing the bulk of the residue to be removed by rubbing off said bulk with elastomeric disks.

5

18. The method of claim 1, wherein said microemulsion comprises by weight:

	5-8%	odorless mineral spirits,
	1-3%	n-propanol,
10	3-5%	30% active laurylamine oxide,
	2-4%	polyethoxylated linear primary alcohol, and
	80-89%	deionized water to total 100%.

15

19. The method of claim 1, wherein said microemulsion comprises by weight:

	12-15%	aromatic mineral spirits,
	1-4%	dipropylene glycol methyl ether,
20	8-12%	30% active laurylamine oxide,
	5-7%	polyethoxylated linear primary alcohol, and
	62-74%	deionized water to total 100%.

25

20. A microemulsion for cleaning silicone wax, grease or grime from hard surfaces comprising by weight:

	5-8%	aliphatic organic solvent,
	1-3%	co-surfactant,
30	3-5%	amine oxide surfactant,
	2-4%	nonionic surfactant having an HLB of between 7.5 and 10, and
	80-89%	deionized water to total 100%.

35

21. A microemulsion for cleaning silicone wax, grease or grime from hard surfaces according to claim 14 comprising by weight:

- 23 -

5
5-8% odorless mineral spirits,
1-3% n-propanol,
3-5% 30% active laurylamine oxide,
2-4% polyethoxylated linear primary
alcohol, and
80-89% deionized water to total 100%.

22. A microemulsion for cleaning adhesives
from hard surfaces comprising by weight:
10 12-15% organic solvent having at least 5%
aromatic or polar components,
1-4% co-surfactant,
8-12% amine oxide surfactant,
5-7% nonionic surfactant having an HLB
15 of between 7.5 and 10, and
62-74% deionized water to total 100%.

23. A microemulsion for cleaning adhesives
from hard surfaces according to claim 15 comprising by
20 weight:
12-15% aromatic mineral spirits,
1-4% dipropylene glycol methyl ether,
8-12% 30% active laurylamine oxide,
5-7% polyethoxylated linear primary
25 alcohol, and
62-74% deionized water to total 100%.

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C11D3/43; C23G5/06						
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%; border-bottom: 1px solid black; padding: 5px;">Classification System</td> <td style="border-bottom: 1px solid black; padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">Int.Cl. 5</td> <td style="padding: 5px;">C11D ; C23G</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched⁸</div>			Classification System	Classification Symbols	Int.Cl. 5	C11D ; C23G
Classification System	Classification Symbols					
Int.Cl. 5	C11D ; C23G					
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹						
Category ^o	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³				
X	EP,A,0 384 715 (COLGATE-PALMOLIVE) 29 August 1990 see page 8, line 45 - page 9, line 9; claims 1-4; example 1 <div style="text-align: center;">---</div>	1,2,4-6, 15,16				
X	EP,A,0 052 275 (DU PONT DE NEMOURS) 26 May 1982 see page 6, line 14 - page 7, line 14; claims; example & US,A,4 446 044 1 May 1984 cited in the application <div style="text-align: center;">---</div>	1-4,11				
A	EP,A,0 368 146 (COLGATE-PALMOLIVE) 16 May 1990 see claims 1-5,18-21; examples <div style="text-align: center;">---</div>	1-23				
A	EP,A,0 337 576 (COLGATE-PALMOLIVE) 18 October 1989 see the whole document <div style="text-align: center;">---</div> <div style="text-align: center;">-/--</div>	1-23				
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>^o Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>						
IV. CERTIFICATION						
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report					
14 AUGUST 1992	21. 08. 92					
International Searching Authority	Signature of Authorized Officer					
EUROPEAN PATENT OFFICE	GRITTERN A.G.					

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 005 309 (DAWLEY BROOK PAPERS LTD.) 14 November 1979 see page 6, line 24 - page 7, line 4; claims; example 22; table 1 ---	1-6,14, 15
A	US,A,3 929 499 (F.L. THOMAS) 30 December 1975 see column 1, line 60 - column 2, line 40; claim ---	1,10,11

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9202760
SA 59268

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 14/08/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0384715	29-08-90	US-A- 4919839	24-04-90
		AU-A- 4917290	30-08-90
		CA-A- 2009155	21-08-90
EP-A-0052275	26-05-82	CA-A- 1170950	17-07-84
		JP-C- 1601435	18-02-91
		JP-B- 2025959	06-06-90
		JP-A- 57111399	10-07-82
		US-A- 4446044	01-05-84
US-A-4446044	01-05-84	CA-A- 1170950	17-07-84
		EP-A, B 0052275	26-05-82
EP-A-0368146	16-05-90	US-A- 5108643	28-04-92
		AU-A- 4438189	10-05-90
		CA-A- 2002267	07-05-90
EP-A-0337576	18-10-89	US-A- 4921629	01-05-90
		AU-A- 3257589	19-10-89
EP-A-0005309	14-11-79	GB-A- 2014182	22-08-79
US-A-3929499	30-12-75	None	